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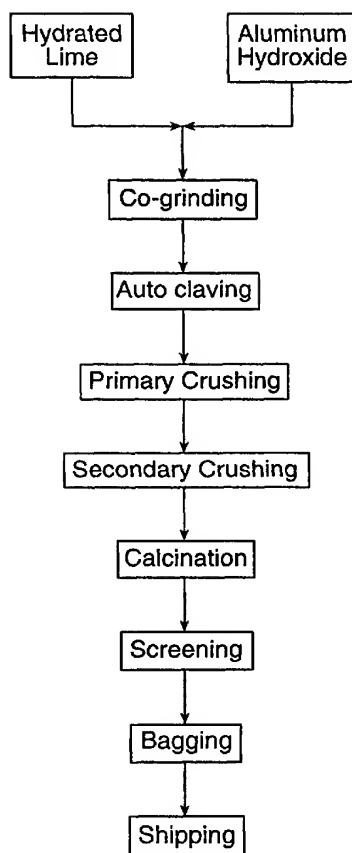
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(54) Title: INSULATING RAW MATERIAL FOR HIGH TEMPERATURE APPLICATIONS



(57) Abstract: A refractory insulating aggregate for high temperature applications has been developed. The product contains approximately 92 % Al_2O_3 and 7.5 % CaO ; its mineralogical composition is calcium hexaluminate. The product is a homogeneous material with a high porosity of typically 75 % and a small pore radius of 0.5-5 μm . The product is produced by a process which includes hydrothermal hardening in an autoclave.



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INSULATING RAW MATERIAL FOR HIGH TEMPERATURE APPLICATIONS

The present invention relates to insulating materials and methods of making refractory bodies.

Insulating materials are important products for many industrial applications. They are used to minimize heat and energy losses and to improve safety of equipment and working environment. Depending on the application, insulating products have to meet various requirements:

- highly efficient thermal insulation properties in order to minimize wall thickness,
- excellent thermal shock resistance,
- easy to handle and safe to install, and
- high durability to minimize downtimes and related costs.

Recent changes in the European legislation have started a new discussion around the health aspect of various insulating products. In December 1997, the European Union classified ceramic mineral fibers as a category 2 carcinogen. This has stimulated an intensive search for alternative products with similar refractoriness, low thermal conductivity, and less concerns around potential health hazards.

The thermal conductivity properties of refractory materials are determined by their heat transport characteristics, which are conduction in solids/gases, convection, and radiation. The kinetics are well known in the art and are explained in detail by Schulle (Feuerfeste Werkstoffe. Dt. Verlag für Grundstoffindustrie, Leipzig, 1990). An article by Seifert, H.: Mikroporöse Feuerbeton-Leichtzuschlagstoffe. Silikattechnik 38 (1987) 4, p. 129-131, specifically discusses the thermal characteristics of microporous materials.

The development of material of the present invention was targeted to obtain an insulating aggregate with high refractoriness for use at temperatures above 1200°C. At high temperatures the major heat transfer mechanism is the radiation. The radiation emission rises with the 4th power of the temperature. Pores behave like a vacuum for radiation (so-called short circuit of pores). Thermal conductivity by radiation is proportional to the pore size. Smaller pore sizes result in a lower radiant heat conductivity. Figure 1 shows an example for two products with similar

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total porosity, but different pore sizes. The product with the smaller pore size has the lower thermal conductivity at high temperatures.

Therefore to provide optimum insulating efficiency, the target microstructure for the new insulating aggregate was that the pore size should be as small as possible to minimize radiation, and that the total porosity should be high. To allow the use at high temperatures, the mineral phase should have a high refractoriness and a low impurity level.

Accordingly, it would be advantageous to provide a replacement material in many of the applications where ceramic fibers are currently used.

An object of the invention is to provide a new insulating aggregate having a small pore size to minimize heat transfer by radiation.

Another object of the present invention is to provide a new insulating aggregate having a high total porosity.

Still another object of the present invention is to provide a new insulating aggregate having a high total porosity.

Other features of the present invention will be further described in the following related description of the preferred embodiment which is to be considered together with the accompanying drawings wherein like figures refer to like parts and further wherein:

Figure 1 is a graph showing the effect of temperature on the thermal conductivity of two refractory materials with similar porosity.

Figure 2 is a graph showing the micro pore distribution of the product of the present invention.

Figure 3 is a scanning electron micrograph of the present invention.

Figure 4 is a graph comparing the thermal conductivity of the present invention to other materials.

Figure 5 is a graph showing the micro pore size distribution of several variations of the present invention.

Figure 6 is a graph showing the refractoriness of the present invention under load curves.

Figure 7 is a graph showing the creep in compression of the present invention.

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Figure 8 is a graph showing the thermal conductivity of the present invention.

Figure 9 is a process flow diagram for making the product of the present invention.

5 The present invention is a refractory insulating product having an alumina content greater than 60%, a density less than 1.5 g/cm^3 , a porosity greater than 50% and a median pore diameter smaller than $15 \text{ }\mu\text{m}$. The material of the present invention is useful for insulation up to high temperatures ($>1400^\circ\text{C}$). Preferably the total impurities of the material of the present invention is less than or
10 equal to 5%. This results in:

- thermal stability against sintering or creep at high temperature usage;
- chemical stability at reducing or alkaline atmospheres (i.e., for petrochemical, glass, ceramics, or ammonia production).

15 In a further aspect of the present invention, the refractory insulating product has an alumina content from greater than 60% to 92% and a CaO content from 8% to less than 20%. The percentages are by weight herein.

 The material of the present invention can be used as a raw material for refractory products or other production processes than run under high energy
20 input, have traditionally used ceramic mineral fibres and need replacement, or have critical working conditions regarding durability of refractory insulating products under high temperature, chemical attack and reducing atmosphere. Examples of such applications are steelworks, foundries, non-iron metal production, cement production, glass production, firing kilns, petrochem industry, chemical industry, or
25 other.

 Another aspect of the invention is the use of hydrothermal hardening of low loose bulk density ($< 1 \text{ t/m}^3$) dry powder compound, followed by crushing, sintering, sizing, and bagging. The hydrothermal hardening is accomplished in an autoclave with saturated steam at $100\text{-}300^\circ\text{C}$, 1-100 bar, 3-50 h. By Autoclaving of
30 dry powder instead of the previously patented slurry route: increased throughput and drastically reduced production costs. The resulting product is a light weight, microporous, high porosity insulating material.

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Physical product properties of the present invention

The term "hydratable alumina" is intended to include an alumina mineral that is already hydrated.

The base mineral composition for material of the present invention is calcium hexaluminate (CA_6 - where $C=CaO$, $A=Al_2O_3$). Theoretical composition:

$$CA_6 = CaO \cdot 6 Al_2O_3 = 91.6\% Al_2O_3, 8.4\% CaO$$

Target is an alumina-rich CA_6 to prevent the formation of calcia-rich, hydratable calcium aluminate-phases (CA , CA_2 , $C_{12}A_7$). CaO content range 7-10%, target 8%.

CA_6 exhibits the most excellent thermal properties of the calcium aluminate system with a melting point above 1850°C. CA_6 has high thermal shock resistance, a thermal expansion and fracture toughness K_{IC} similar to alumina, moderate flexural strength due to anisotropic grain growth, and stability in reducing atmosphere. In addition, European Patent Application EP 0 615 959 A1 reports that calcium aluminate-based material have good stability in contact with alkali oxides.

Table 1 shows that the product chemistry of material of the present invention.

Chemical Composition	Unit	Typical	Min.	Max.
Al_2O_3	%	92.5-93.5	91	
CaO	%	6-7		8
Na_2O	%	0.2-0.4		0.5
SiO_2	%	0.05-0.07		0.1
Fe_2O_3	%	0.03-0.04		0.1
MgO	%	0.05-0.3		0.4
Bulk Density	g/cm^3	0.65-0.7		0.75

In comparison to the present invention, pure CA_6 is 91.6% Al_2O_3 , 8.4% CaO . The present invention is on the alumina-rich side in order to suppress the formation of hydratable calcium aluminate phases (CA , CA_2). The impurity level is low, SiO_2 and Fe_2O_3 contents are max. 0.1%. The bulk density is around 0.65-0.7 g/cm_3 .

Figure 2 is a graph showing the micro pore distribution of the

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product of the present invention. The micro pore size distribution in Figure 2, as measured by Hg-intrusion method, shows a narrow range of 1-5 μm with an average pore size of 3-4 μm .

Figure 3 is a scanning electron micrograph of the present invention.

5 The scanning electron microscope image in Figure 3 shows the microporous, homogeneous internal structure of the material of the present invention. The interlocking nature of the platelet-shaped CA_6 -crystals results in a high level of internal porosity (typically 75%), as well as enhancing the strength of the aggregates. The free distance between the CA_6 -platelets determines the small pore
10 diameter.

The material of the present invention is produced via a wet chemical process which includes sintering of the final product at high temperatures. Its performance has been evaluated at temperatures up to 1500°C. The material of the present invention is produced in four sizes, three closed sizes (1-3, 3-6, 6-10 mm)
15 and one open (0-1 mm). The loose bulk density is around 400 kg/m^3 for the closed sizes and around 700 kg/m^3 for the fine fraction.

Thermal conductivity of material of the present invention grains

The thermal conductivity of 1-3 and 3-6 mm material of the present invention grains was tested in the form of beds with packed density. Testing was
20 done up to 1400°C according to the hot wire method (parallel wire) (DIN EN 993-15). The packing density of the grain bed was achieved by densification of the loose fill through tapping.

Figure 4 is a graph comparing the thermal conductivity of the present invention (listed as SLA-92) to other materials. These other materials are
25 commercially available bubble alumina, insulating fire clay grains, and ceramic fiber blanket. As shown in Figure 4, at 25°C, material of the present invention has a thermal conductivity of 0.15 $\text{W/m}\cdot\text{K}$ which gradually rises up to 0.5 $\text{W/m}\cdot\text{K}$ at 1400°C. The curve of the ceramic fiber blanket runs parallel to that of SLA-92, the distance between both lines is approx. 0.15 $\text{W/m}\cdot\text{K}$.

30 Both the bubble alumina as well as fire clay grain bed have a rapid rise of thermal conductivity from 600°C up to 1400°C. The thermal conductivity of the bubble alumina bed is much higher than that of material of the present invention

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over the entire temperature range. The data illustrates the large effect that pore size has on thermal conductivity. The pore size of bubble alumina is nearly equivalent to the grain diameter which is in the mm-range, whereas material of the present invention shows microporosity in the μm -range. This leads to much lower thermal conductivity of material of the present invention especially in the high temperature range where the conductivity is dominated by radiation. The different packed densities of material of the present invention 1-3 and 3-6 mm (0.61 vs. 0.47 g/cm³) have no effect on the thermal conductivity.

The material of the present invention in insulating products

The material of the present invention is currently under evaluation in several applications, where low weight of the castables, refractoriness and thermal insulation properties are key factors. High purity is essential in applications such as petrochemical and ammonia industry to provide a product with CO- and alkali resistance.

Brick pressing trials of the material of the present invention showed that the grain crushing strength is sufficient for insulating brick production. The relatively high grain strength also provides grain stability when the mix casting is helped by ramming or poking. Ease of installation as well as of destruction leads to shorter down times and helps to reduce costs. The porosity of material of the present invention provides good stickiness for gunning.

Examples

The tests described above give some examples for the application of material of the present invention aggregate in castables or bricks and show the physical and insulating properties of the refractory products produced from this aggregate.

The composition of the Test Mix 16/1 castable is shown in Table 2.

Mix 16/1 Castable	
Invention (grain)	70%
Cement CA 25R	30%
Additives	+1%
0,5% cellulose solution	+60%

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Preparation and treatment of the test pieces and testing followed the European standard DIN ENV 1402 "Unshaped refractory products", Part 5 and Part 6.

The dry ingredients were mixed for 1 minute. After addition of 60% of a solution with 0.5% cellulose (Blanose ex Aqualon/Henkel), the mixing was continued for another 4 minutes. The castable was cast under vibration into the mould. Vibration time was 30-60 sec with an amplitude of 0.2-0.5 mm depending on the specimen size.

The following test pieces were prepared:

- 230 mm x 64 mm x 54 mm for testing the conventional properties (DIN ENV 1402-6)
- 230 mm x 114 mm x 64 mm for testing thermal conductivity (hot-wire (parallel) method DIN EN 993-15)
- 150 mm x 25 mm x 25 mm for testing the hot modulus of rupture (DIN EN 993-7)

The vibrated test pieces were cured at room temperature in the mold for 24h and after de-molding for another 24h in air with a relative humidity of $\geq 90\%$. The pieces were dried for 24h at 110°C and fired from 850°C up to 1500°C with a soaking time of 5h.

For the brick preparation the same composition as for the vibration castable (Table 2) was used, but only 30% of the cellulose solution was added. Bricks (250 mm x 100 mm x 65 mm) and plates (250 mm x 100 mm x 30 mm) were pressed without problems on an industrial hydraulic press with an applied pressure of 0.2 N/mm². Edges and corners of the pressed pieces are strong enough for an automatically transport. The modulus of rupture of the green pressed plates is about 0.8 N/mm².

The physical properties of the prepared test pieces after drying and firing up to 1500°C are compiled in Table 3 below.

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	Unit	Pre-Treatment (°C)	Mix 16/1 Castable	Mix 16/1 Brick
Permanent linear change	%	110 850 1000 1400 1500	- 0.05 - 0.04 - 0.08 - 0.44 - 0.95	- 0.02 - 0.04 - 0.06 - 0.40 - 0.77
Bulk density	g/cm ³	110 850 1000 1400 1500	1.19 1.10 1.08 1.07 1.12	1.42 1.29 1.28 1.27 1.32
Open porosity	Vol. %	110 850 1000 1400 1500	62.7 70.9 71.3 68.6 66.8	55.5 65.8 66.0 62.0 60.6
Cold modulus of rupture CMOR	N/mm ²	110 850 1000 1400 1500	0.33 0.27 0.24 0.6 0.98	1.1 0.9 1.2 2.2 2.6

	Unit	Pre-Treatment (°C)	Mix 16/1 Castable	Mix 16/1 Brick
Cold crushing strength CCS	N/mm ²	110 850 1000 1400 1500	2.2 3.1 3.7 3.7 6.5	8.7 8.5 8.9 10.3 11.5
Hot modulus of rupture HMOR	N/mm ²	1400 1500	1.0 1.9	n.d.
Thermal expansion at 1000°C	%	1500	0.79	0.76
Refractoriness under Load T _{0.5} (0.05 N/mm ²)	°C	1500	1485	1495
Thermal shock resistance (air)	cycles	1400 1500	>10 >10	10 n.d.
Gas permeability	nPm	1400 1500	- 5.4	5.1 -

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The drying shrinkage of the Mix 16/1 is about 0.05 % and the firing shrinkage at 1400°C/5h reaches about 0.4 % for both castable and pressed brick. The firing temperature of 1500°C results in a shrinkage of 0.95 % for the castable and 0.77 % for the pressed brick

5 There is practically no change in bulk density and open porosity at firing temperatures from 850 up to 1400°C. In this temperature range the castables has a bulk density of about 1.1 g/cm³, the pressed brick of about 1.28 g/cm³. The apparent porosity is about 70 % for the castable and 66% for the pressed brick. The slightly higher shrinkage at 1500°C results in a small increase of bulk density
10 and decrease in porosity.

 Figure 5 is a graph showing the micro pore size distribution of several variations of the present invention. The total microporosity is roughly 60%. Even at firing at 1500°C the median pore diameter of the Mix 16/1 material remains at about 3-5 µm similar to that of the material of the present invention grain, but
15 the castable and the brick contain a small amount of larger pores up to 60 µm.

 The gas permeability of the fired 16/1 castable and pressed brick at 1400-1500°C is in the range of about 5.5 nPm, a relatively low value for these high porous materials. The low value is the effect of the very small pore size.

 Up to a firing temperature of 1000°C, the flexural strength remains at
20 about 0.3 N/mm² for the castable and about 1 N/mm² for the pressed brick because of its higher bulk density. Firing temperature of 1500°C increases strength about a factor of three.

 The development of cold crushing strength is similar to the changes in the cold modulus of rupture. After firing at 1500°C, the cold crushing strength
25 reaches 6.5 N/mm² for the castable and 11.5 N/mm² for the pressed brick.

 The test results indicate that the modulus of rupture from room temperature up to 1500°C testing temperature remains constant at about 1 N/mm², emphasizing that no melting phase in the material develops.

 Figure 6 is a graph showing the refractoriness of the present
30 invention under load curves (DIN EN 993-8) of pre-fired specimen of Mix 16/1 castable and brick. The pressed brick pre-fired at 1400°C reaches practically the same high T_{0,5} value as the 1500°C pre-fired castable of about 1490°C.

Figure 7 is a graph showing the creep in compression of the present invention. From the creep curves (DIN EN 993-9) in Figure 7 the test results as given in Table 4 below were calculated. They demonstrate the good creep resistance of material of the present invention materials up to 1400°C.

Mix 16/1	Pre-Firing (°C)	Creep Test Temperature (°C)	Applied Load (N/Mm ²)	Deformation From 5 th -25 th H (%)
brick	1400/5h	1300	0.05	0.2
castable	1500/5h	1400	0.05	0.7

The air quenching method, according to DIN ENV 993-11 was used to determine thermal shock resistance. The thermal shock test was stopped after 10 cycles and the strength measured and compared to the untreated material. The results are reported in Table 5 below and show that the Mix 16/1 castable fired at 1000°C up to 1500°C shows no sign of cracks and no strength decrease after 10 cycles.

			Cold Modulus of Rupture (N/mm ²)		Cold Crushing Strength (N/mm ²)	
	pre-firing (°C)	cycles to failure	before	after 10 cycles	before	after 10 cycles
Mix 16/1 castable	1000	> 10	0.24	0.30	3.7	3.5
	1400	> 10	n.d.	n.d.	n.d.	n.d.
	1500	> 10	0.6	1.1	6.5	6.1

The pressed brick fired at 1400°C failed at 10 cycles by one crack passing through the material, probably due to the higher density of the material or not yet optimized pressing parameters when forming the brick (laminations).

Figure 8 is a graph showing the thermal conductivity of the present invention (Mix 16/1) castable and pressed brick. For the materials pre-fired to 1000°C, the thermal conductivity decreases from 25°C down to 500°C and then levels out in the temperature range from 800°C to 1300°C at about 0.4 W/m·K. Pre-firing at 1300°C results in a steady decrease of thermal conductivity from 0.5 W/m·K to 0.4 W/m·K. The differences of thermal conductivity between castable

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and brick are small, even though the brick has a higher bulk density.

The Mix 16/1 material competes with the thermal conductivity of high temperature insulating bricks. The increasing thermal conductivity of ceramic fiber modules at 1300°C leads to values similar or higher as the Mix 16/1 material.

5 In Table 6 below selected properties of the Mix 16/1 castable pressed brick are compared to two just available refractory materials for high temperature insulating applications: a bubble alumina castable and an insulating mullite brick (Group ASTM 30).

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	Unit	Mix 16/1 Castable (1400°C ³)	Mix 16/1 Brick (1400°C)	Bubble Alumina Castable (1400°C)	Insulating High Alumina Brick
Al ₂ O ₃ /CaO	%	89/10	89/10	96/3	73/-
Bulk density	g/cm ³	1.07	1.27	1.50	1.08
Open porosity	vol.%	68.6	62.0	48	66.7
Gas permeability	nPm	5	5.3	0.8	160
CMOR (20°C)	N/mm ²	0.6	2.6	5	1.6
HMOR (1400°C/5h)	N/mm ²	1	n.d.	4.9	0.4
CCS (20°C)	N/mm ²	3.7	10.3	15	2.5
RuL T _{0.5} N/mm ²	°C	(1500°C) 1485	1495	(1500°C) 1565	1485
Permanent linear shrinkage	%	- 0.44	- 0.4	- 0.3	+ 0.4
Thermal shock resistance (air)	cycles	> 10	10	2	6
Thermal conductivity (1000°C)	W/m·K	0.4	0.4	- 0.6	0.5
Creep test (1400°C)	% 5 th -25 th h	(1500°C) 0.7		(1500°C) 0.2	2.7

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It is to be noted that the two other products can only give a rough comparison because of the wide variety of the properties of these two refractory product types.

The material of the present invention which includes the concept of an optimized insulating aggregate for high temperatures with a high porosity and a small pore size, has shown to give the targeted low thermal conductivity up to 1300°C.

Tests with material of the present invention as a grain bed showed a slow rise in thermal conductivity up to 1300°C, an effect of its microporosity. A similar slow rise in thermal conductivity was seen for the ceramic fiber blanket, its conductivity was at approx. 0.1-0.15 W/m·K lower. This correlation could indicate some future potential. The tested bubble alumina and fire clay grain beds had a distinctly higher and steeper rising thermal conductivity in the critical high temperature range above 600°C where radiation becomes the main contributor to thermal conductivity.

The material of the present invention Mix 16/1 based test castable and brick showed good hot properties up to the tested 1400-1500°C, which reflects the stability of the product and its low impurity level. Thermal shock cycling revealed excellent stability of the material of the present invention castable after 10 cycles, a similar specimen remained undamaged after 20 cycles in a separate external test.

The brick had a higher strength and lower creep rate than the castable due to higher densification (fired 1000°C: 1.08 vs. 1.28 g/cm³), but still the thermal conductivity properties of the brick were similar to the lighter castable. This again shows that the microporosity is the major contributor to the insulating properties.

An important characteristic of the material of the present invention Mix 16/1 materials is the constant low thermal conductivity level with little or no rise up to 1300°C, where an average value of 0.4 W/m·K is found. This indicates competitiveness of its properties to high temperature insulating bricks. The increasing thermal conductivity of ceramic fibers modules at 1300°C lead to values similar or higher as the Mix 16/1 material, a finding which could open up some future potentials for material of the present invention.

The material of the present invention presents a new concept for

insulating aggregates with a high potential for high performance, innovative insulating products. It could be the key to new solutions for technical requirements such as decreased lining thickness, longer lifetime, increased volume/capacity, higher operating temperatures, or higher energy savings.

5 The new insulating aggregate of the present invention can be an alternative material for existing insulating products. Its benefits include high creep resistance, high thermal shock resistance, high purity, and low thermal conductivity at temperatures above 1200°C. It seems to have a potential to be a replacement material in many applications that currently use ceramic fibers. The material of the present invention could assist in alternative products solutions with similar
10 refractoriness, low thermal conductivity, and fewer concerns around potential health hazards.

Figure 9 is a process flow diagram for the present invention.

Raw Materials

15		<u>Oxide content</u>	<u>finer than</u>	<u>d50</u>
	Calcium Hydroxide Ca(OH) ₂	73.55 % CaO	63 µm	20 µm
	or Calcium oxide CaO	>95% CaO	63 µm	20 µm
	Aluminium Hydroxide Al(OH) ₃	65.20 % Al ₂ O ₃	32 µm	10 µm

Raw Mix Composition

Mixing ratio: 100 kg Al(OH)₃ + 6.66 kg Ca(OH)₂ --> 7% CaO
+ 7.70 kg Ca(OH)₂ --> 8% CaO

Grinding

The grinding in the process shown in Figure 9 is to produce a high fineness so as to achieve high loose bulk density of the raw mix of $<1 \text{ t/m}^3$. This results in low density, small pore size and high porosity of final product.

Filling of autoclaving forms

Filling under high agitation of dry powder to full desagglomeration and to generate free flowability. Optional spraying of water mist in layers during filling on powder and on top (stabilizes bulk density) and/or granulation to balls with water and filling of forms therewith (stability/pre-sizing of aggregates/optimum usage of autoclaving capacity).

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Autoclaving

Autoclaving conditions: saturated steam at 100-300°C, 1-100 bar, 3-50 h holding time. Hardens/solidifies dry powder to solid body with consistency of soft to hard chalk.

5

Crushing

Crushing autoclaved material close to the requested final product size (0.2 mm to <10 mm). Crushers must be suitable to downsize chalky material without grinding, smearing, or other destruction of the product structure.

Conversion/Sintering

10

Heat treatment is performed in kiln with high end temperature. The target temperature for sintering is greater than 1500°C.

Screening, Bagging, Shipping

Final screening to desired final aggregate sizes, bagging and shipment to consumers.

15

The key step in the method of the present invention is the autoclaving step. The ground material is hydrothermally hardened in an autoclave with saturated steam at 100-300°C, 1-100° bar, 3-50 h.

The performance of material of the present invention is suited to higher application temperatures. The option for the development of the family of insulating raw materials with different chemistries is under evaluation for the future. Members of the family include:

20

(a) calcium hexaluminate CA_6 $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$

(b) corundum Al_2O_3

(c) MA-Spinel $\text{MgO} \cdot \text{Al}_2\text{O}_3$

25

(d) beta-alumina $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ (also contains LiO_2 , K_2O , CaO , BaO)

(e) mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$

(f) aluminum titanate $\text{Al}_2\text{O}_3 \cdot \text{TlO}_2$

30

The invention is obviously not limited to the embodiments just described, and numerous changes and modifications can be made to the latter without departing from the scope of the invention.

The refractory insulating aggregate can be used in insulating

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applications in form of loose grain filling, castables, or bricks. Examples for refractory applications include i.e. the heat insulating cover of ladles for secondary metallurgy or of steel tundishes, the heat insulation of the walls of ladles for secondary metallurgy, for heat insulation in reheat furnaces for steel milling, 5 refractories for aluminum industry such as secondary runners or roofs of remelting furnaces, insulation linings and kiln car refractories for kilns for firing of ceramics, refractories for petrochemical industry, or refractories for chemical industry.

What is believed to be the best mode of the invention has been described above. However, it will be apparent to those skilled in the art that 10 numerous variations of the type described could be made to the present invention without departing from the spirit of the invention.

C L A I M S

1. A refractory insulating aggregate for high temperature, the composition of said aggregate comprising more than about 80% Al_2O_3 and less than about 20% CaO.
- 5 2. The refractory insulating aggregate of claim 1 in which said composition is an alumina-rich calcium hexaluminate containing mineral side phases 0-30% alphaalumina ($\alpha\text{-Al}_2\text{O}_3$), 0-30% $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ (CA2), and 0-10% $\text{CaO}\cdot \text{Al}_2\text{O}_3$ (CA).
3. The refractory insulating aggregate of claim 1 in which said
10 composition comprises about 90 to about 94% Al_2O_3 .
3. The refractory insulating aggregate of claim 1 in which said composition comprises about 7 to about 10 % CaO.
4. The refractory insulating aggregate of claim 1 in which said aggregate has porosity greater than about 50%.
- 15 5. The refractory insulating aggregate of claim 1 in which said aggregate has a small pore radius of 0.5-5 μm .
6. The refractory insulating aggregate of claim 1 in which said aggregate has an average thermal conductivity of less than 0.5W/m K.
7. The refractory insulating aggregate of claim 1 in which composition
20 has a bulk density of lower than 1.5 g/cm^3 , preferably 0.5-0.9 g/cm^3 .
8. A method a making a refractory insulating aggregate comprising:
 - (a) forming a mixture of a hydratable alumina and at least one member of the group selected from calcium oxide and calcium hydroxide;
 - (b) grinding said mixture;
 - 25 (c) thermally autoclaving said mixture to form a solid body;
 - (d) crushing said solid body to form a plurality of particles having a size of less than about 15 mm; and
 - (e) sintering said plurality of particles.
9. The method of claim 8 in which (c) further comprises spraying said
30 mixture with water prior to autoclaving.
10. The method of claim 8 in which (c) further comprises thermally hardening said mixture with saturated steam at a temperature between about 100°C

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and about 300°C.

11. The method of claim 8 in which (c) further comprises thermally hardening said mixture with saturated steam at a temperature between about 100°C and about 300°C at a pressure of between about 1 to about 100 bar.

5 12. The method of claim 8 in which (e) further comprises sintering said plurality of particles at a temperature greater than about 1000°C.

13. The method of claim 8 in which (e) further comprises sintering said plurality of particles at a temperature greater than about 1400°C.

14. The method of claim 8 in which (e) further comprises sintering said
10 plurality of particles to form an aggregate with particles group selected from calcium hexaluminate ($\text{CaO} \cdot 6\text{Al}_2\text{O}_3$), corundum (Al_2O_3), MA-Spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$), beta-alumina ($\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), aluminum titanate ($\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$) and mixtures thereof.

15. The method of claim 8 in which (e) further comprises sintering said
15 plurality of particles to form an aggregate with particles group selected Li_2O , K_2O , CaO , BaO and mixtures thereof.

16. A refractory insulating aggregate for high temperature, the composition of said aggregate comprising an alumina-rich calcium hexaluminate containing about 92 to about 94% Al_2O_3 .

20 17. The refractory insulating aggregate of claim 16 in which said alumina-rich calcium hexaluminate comprises about 7 to about 8 % CaO .

18. The refractory insulating aggregate of claim 16 in which said aggregate has porosity greater than about 50%.

19. The refractory insulating aggregate of claim 16 in which said
25 aggregate has a small pore radius of 0.5-5 μm .

20. The refractory insulating aggregate of claim 16 in which said aggregate has an average thermal conductivity of less than 0.5W/m K.

21. A method a making a refractory insulating aggregate comprising:

- (a) forming a mixture of a hydratable alumina and at least one
30 member of the group selected from calcium oxide and calcium hydroxide;
(b) grinding said mixture;
(c) hydrothermally hardening said mixture with saturated steam at a

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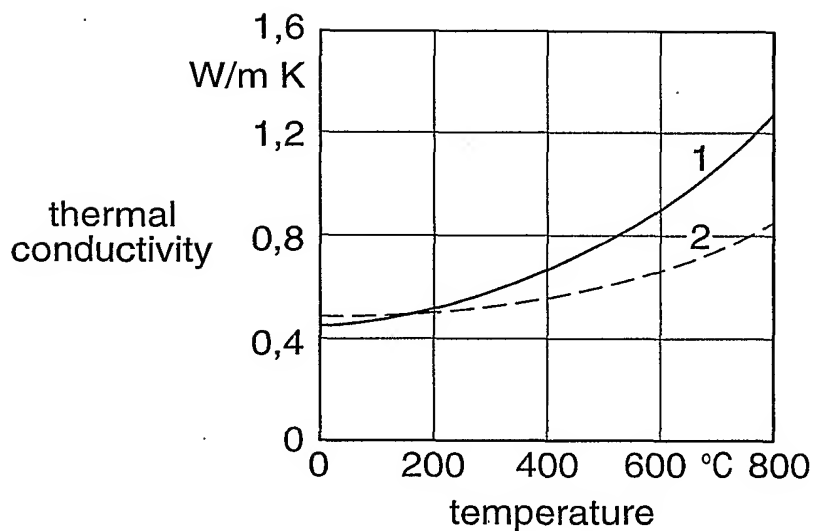
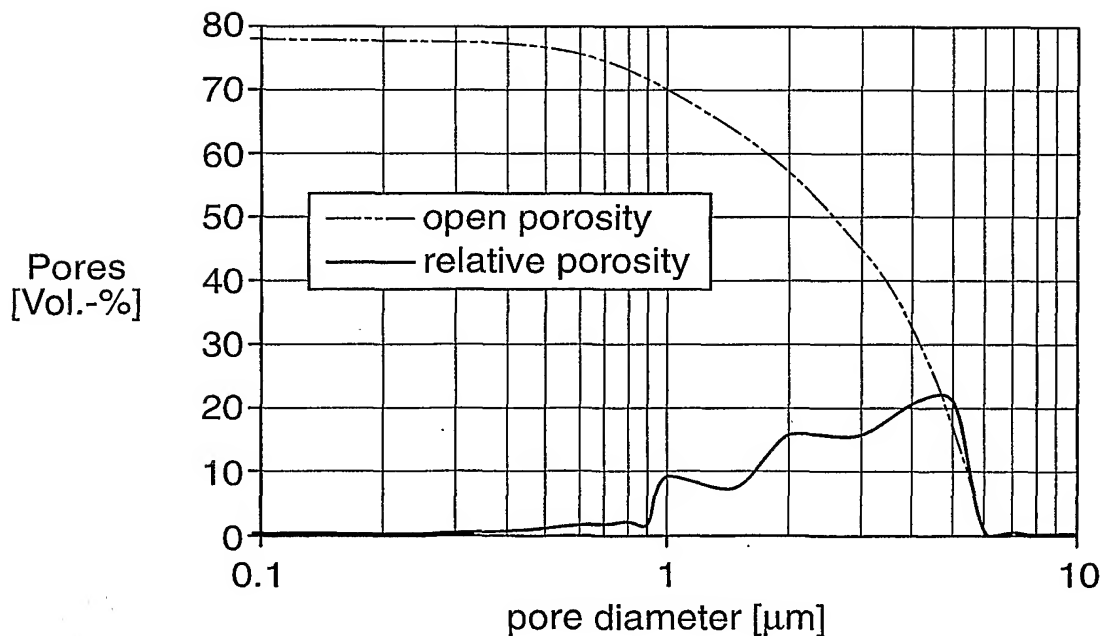
temperature between about 100°C and about 300°C to form a solid body;

(d) crushing said solid body to form a plurality of particles having a size of less than about 15 mm; and

(e) sintering said plurality of particles at a temperature greater than
5 about 1000°C.

22. The method of claim 20 in which (e) further comprises sintering said plurality of particles to form an aggregate with particles group selected from calcium hexaluminate ($\text{CaO} \cdot 6\text{Al}_2\text{O}_3$), corundum (Al_2O_3), MA-Spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$), beta-alumina ($\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), aluminum titanate
10 ($\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$) and mixtures thereof.

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FIG. 1**FIG. 2**

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FIG. 3

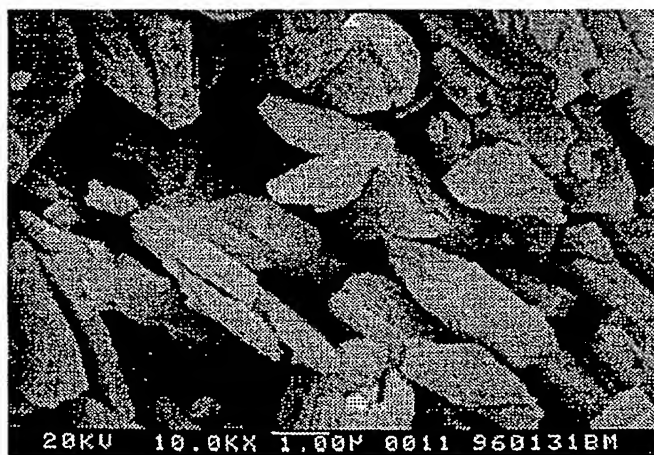


FIG. 4

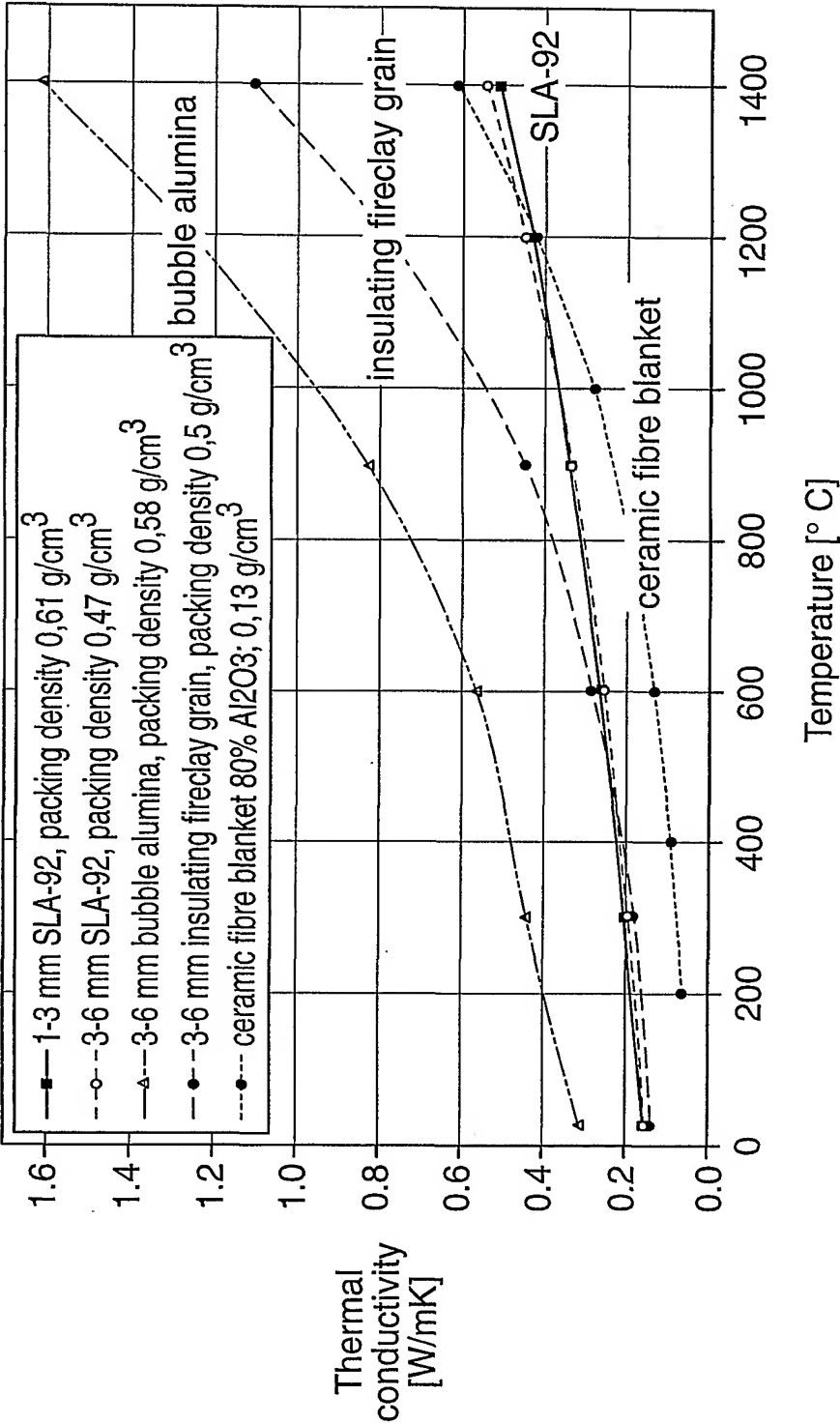


FIG. 5

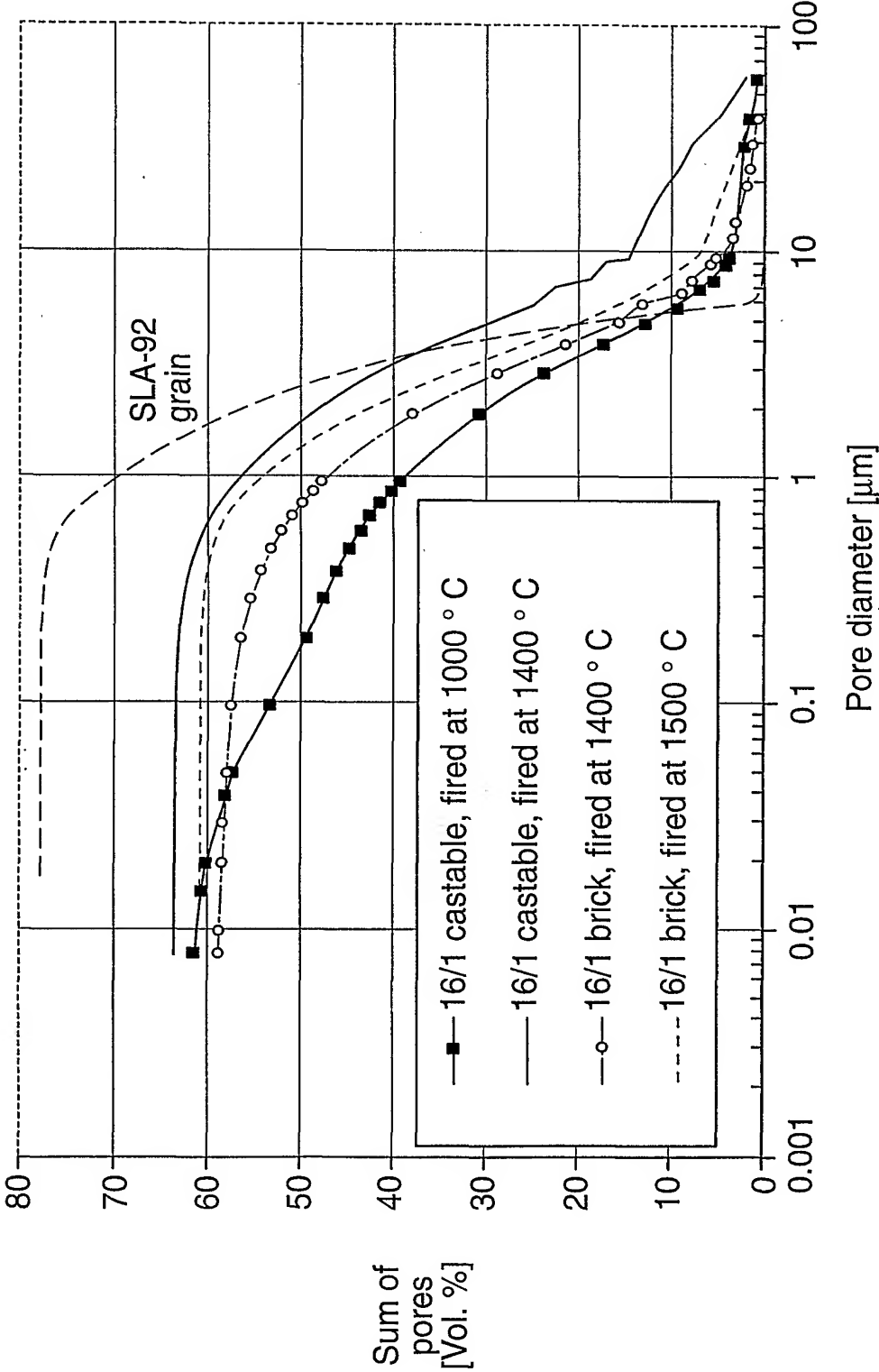


FIG. 6

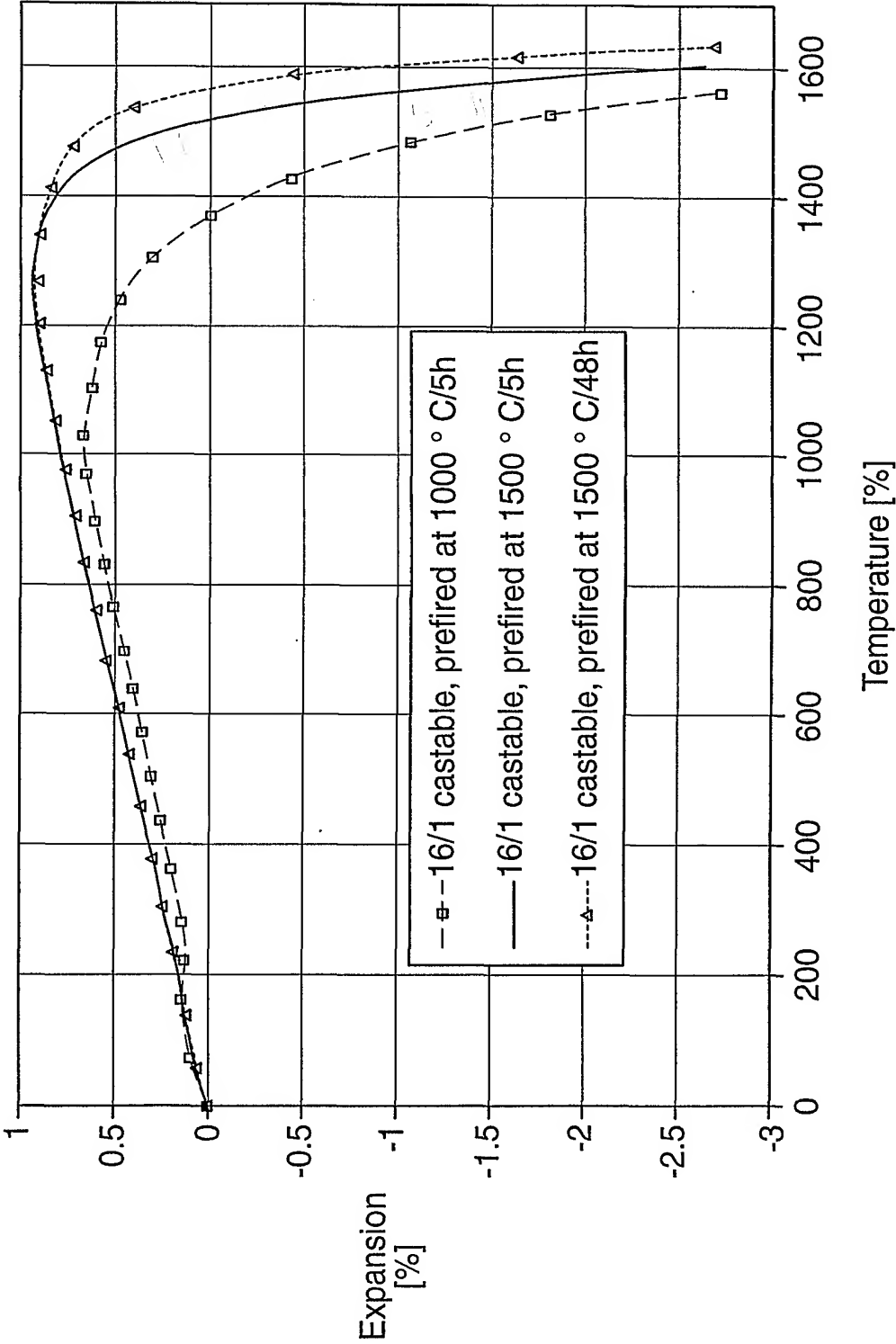


FIG. 7

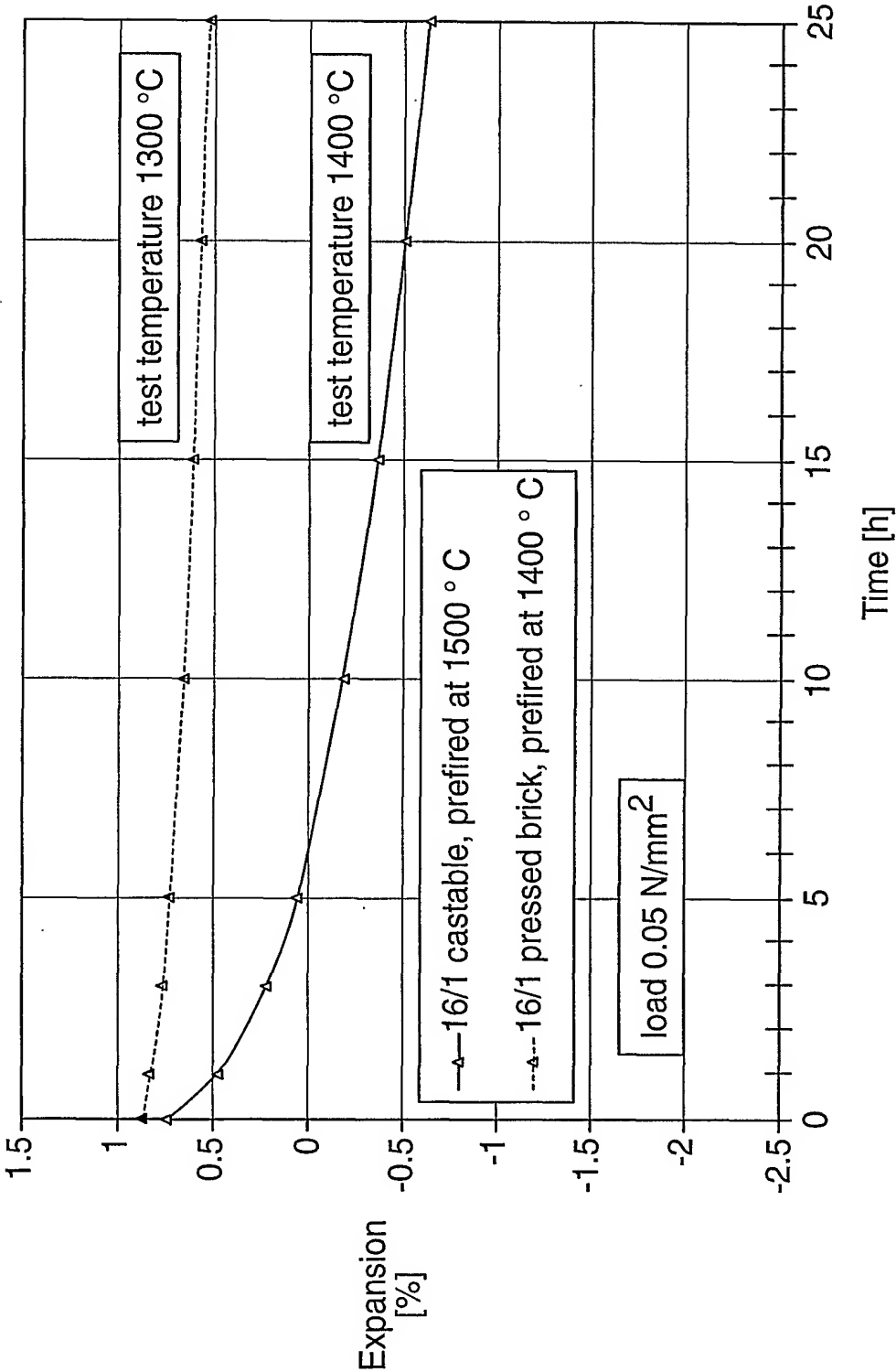
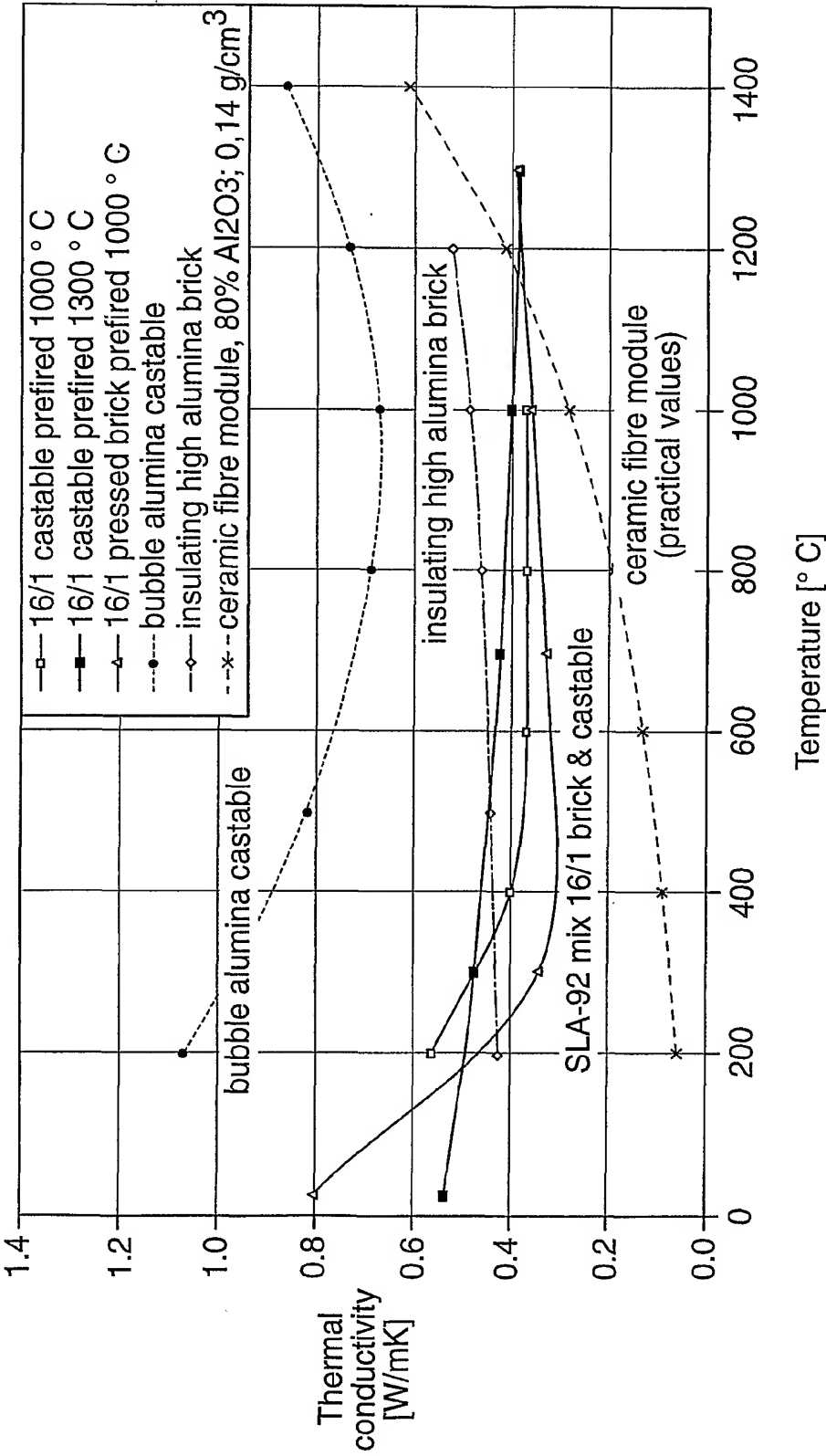
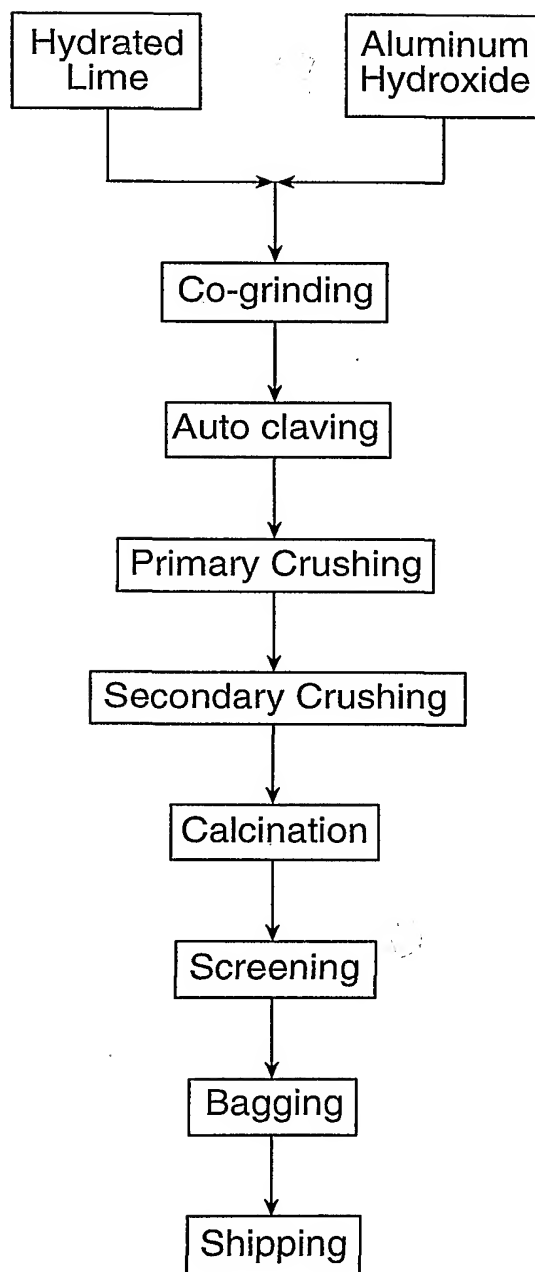


FIG. 8



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FIG. 9

INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/EP 01/06046

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C04B38/00 C04B14/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 92 00928 A (MAGINDAG STEIRISCHE MAGNESIT-INDUSTRIE AG) 23 January 1992 (1992-01-23)	1-7, 16-20
A	abstract; claims 2,3,5; examples 1-3; table 1	8-15,21, 22
A	---- H. SEIFERT: "Mikroporöse Feuerbeton-Leichtzuschlagstoffe" SILIKATTECHNIK, vol. 38, no. 4, 1987, pages 129-131, XP002177800 cited in the application page 129, column 2; tables 1,3,4 page 130, column 1, paragraph 8 page 130, column 2, paragraph 7 -----	1-22

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

19 September 2001

Date of mailing of the international search report

08/10/2001

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Information on patent family members

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